Electrochemistry of Nanoporous Graphene for Lithium-Oxygen Batteries

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論文内容要約

Non-aqueous rechargeable lithium-oxygen ($Li-O_2$) batteries are emerging as a new paradigm for high-density electrical energy storage because of the ultrahigh theoretical energy density (3,500 Wh/kg). Basing on the reversible redox reaction of $2Li + O_2 \leftrightarrow Li_2O_2$, $Li-O_2$ batteries release electrochemical energy by reducing gaseous oxygen from the atmosphere to form insulating solid Li_2O_2 in discharging and are recovered by oxidizing/decomposing Li_2O_2 in charging. Since multi-phases (gas, liquid, solid) are involved into the $Li-O_2$ battery reactions, the cathodes are expected to have open porosity, high conductivity and high catalytic activity, together with good electrochemical stability, light weight and mechanical flexibility. Developing high performance porous cathodes that facilitate highly efficient O_2/Li_2O_2 redox reactions in the aprotic media is very critical for the practical implementation of non-aqueous $Li-O_2$ batteries. In this backdrop, the present thesis work aims to develop advanced three-dimensional (3D) nanoporous graphene materials, and on basis of understanding the fundamental electrochemistry of the cathodic reactions, to develop high-performance nanoporous graphene based $Li-O_2$ batteries.

A nanoporous metal based chemical vapor deposition (CVD) method was employed for synthesizing the novel 3D bicontinuous nanoporous graphene materials. Briefly, nanoporous Ni prepared by dealloying a $Ni_{30}Mn_{70}$ sheet was used as both catalyst and porous template for the CVD growth of graphene at 800-1000 ℃ using benzene, pyridine or thiophene as the precursor. Free-standing nanoporous graphene sheets were obtained after dissolving the nanoporous Ni substrates with hydrochloric acid and then dried by supercritical CO_2. The samples were systematically characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), surface area tests, and physical property measurements. The nanoporous graphene possesses unique properties of interconnected open porosity (> 95%), large accessible surface area (ca. 700-1200 $m^2 g^{-1}$) and high conductivity (ca. 1.2×10^4 S m^{-1}). By using different organic precursors for graphene growth, heteroatoms of nitrogen and sulfur have been successfully doped into the nanoporous graphene to functionalize its catalytic properties. The nanoporous metal based CVD method also provided flexibility in tailoring the pore sizes (200-1000 nm) and dimensions (with thickness ranging from 5 to 100 μm) of the

nanoporous graphene by changing the graphene growth or pre-annealing temperatures and using $Ni_{30}Mn_{70}$ sheet with different dimensions.

A non-aqueous three-electrode electrochemical system, which consists of a disk working electrode, a lithium metal counter electrode and a non-aqueous silver quasi-reference electrode, was developed and utilized for investigating the fundamental Li-O_2 electrochemistry in Li-O_2 battery cathodes. Cyclic voltammetry study showed that the reduction of O_2 to Li_2O_2 proceeds by multi-step reactions via the formation of a LiO_2 intermediate; while in the oxygen evolution reaction (OER), Li_2O_2 is directly oxidized to oxygen without going through LiO_2. Rotating disk electrode measurements further confirmed the formation of a LiO_2 intermediate in the oxygen reduction reaction (ORR). It was also demonstrated that the LiO_2 formation process determines the kinetics of ORR and has a Tafel slope of 120 mV dec^{-1}. The effect of chemical doping on the reaction kinetics of nanoporous graphene for Li-O_2 battery was also investigated by cyclic voltammetry, rotating disk electrode measurements and electrochemical impedance spectroscopy. It was shown that chemical doping by N and S can enhance the catalytic activity of nanoporous graphene for Li-O_2 reactions: N-doping obviously enhances the ORR kinetics and S-doping promotes the OER activity.

The bicontinuous nanoporous graphene was successfully used as cathodes for rechargeable Li-O_2 batteries. Experimentally the centimeter-sized free-standing and flexible nanoporous graphene sheet was directly installed into a Li-O_2 battery without the requirements of complex assembly and binder. With a 1.0 M LiTFSI in tetraethylene glycol dimethyl ether (TEGDME) electrolyte, the Li-O_2 batteries delivered large and recoverable capacities up to ca. 10,400 mAh g^{-1}. A combination of X-ray diffraction (XRD), SEM and TEM characterizations confirmed that the large recoverable capacity is based on highly reversible Li_2O_2 formation and decomposition reactions. The unique bicontinuous porous structure of nanoporous graphene also benefits efficient diffusion of oxygen and ions, giving rise to full utilization of the porosity and very uniform distribution of Li_2O_2 particles in the electrode after discharge. The efficient mass transport also results in a weak dependence of the battery performance on the cathode thickness. It has been shown that chemical doping of nanoporous graphene has an obvious effect on the battery property. N-doping gives rise to a very large discharge capacity and S-doping favors a stable cycling behavior. The nanoporous S-doped graphene based Li-O_2 battery delivers an excellent cycling stability of long lifetimes up to 300 discharge-charge cycles at the cut-off capacity of 1000 mAh g^{-1} and 100 cycles at 2000 mAh g^{-1}, which correspond to the total working time of 2000 and 1333 hours, respectively. The outstanding property of the S-doped graphene benefits from high stability of the sulfur dopants, enhanced reaction kinetics of Li_2O_2 oxidation, and the slow accumulation of side products.

In an effort to develop a full-performance Li-O_2 battery, the nanoporous graphene electrode was further integrated with a

compatible redox mediator. Cyclic voltammetry studies demonstrated the effective role of tetrathiafulvalene in facilitating the decomposition of Li_2O_2 at a significantly decreased charge potential. Stable cycling up to 100 discharge-charge cycles at large capacities (up to 2000 mAh g^{-1}), high rates (up to 2000 mA g^{-1}) and a low charge potential (~3.5 V) have been simultaneously realized in a single Li-O_2 battery. The tetrathiafulvalene-induced low charge potential has also given rise to much less side reactions in comparison with those in the absence of redox mediator, as evidenced by the significantly reduced amounts of alkylcarbonate and Li_2CO_3 in the nanoporous graphene cathode after long cycling tests. To demonstrate the capability of practical implementation of the nanoporous graphene based Li-O_2 batteries, a Li-O_2 pouch battery prototype with a size of about 28 mm × 40 mm × 1.4 mm was developed. Two pieces of large sized nanoporous graphene sheets were assembles face-to-face as the cathodes, with a Li metal foil sandwiching between them as the anodes. The Li-O_2 pouch cells well resemble the excellent properties that have been achieved with coin cells, deliver robust discharge/charge cycling at 1000 mAh g^{-1} and 1000 mA g^{-1} for 100 cycles with quasi-constant discharge/charge potentials and high energy efficiency. Remarkably, the Li-O_2 pouch battery prototype affords a large maximum discharge capacity of 26,840 mAh g^{-1} at a rate of 200 mA g^{-1}, which, when normalized by the total mass of the pouch cell, corresponds to a gravimetric capacity of 95.70 mAh g^{-1}_{cell} and an energy density of 260.30 Wh kg^{-1}_{cell}, surpassing those of commercial Li-ion polymer batteries.